Biomimetic Electroreduction of nitrite by Hemin, Myoglobin and Hemoglobin in Surfactant Films

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Nitrite is an important source of nitrogen in green plants and its complete reduction is achieved in nature by nitrite reductase enzymes which contain complex proteins having an iron-sulfur unit and an iron isobacteriochlorin (1). In this context, the desire to mimic the enzymatic systems has led to an active area of research involving synthetic porphyrin models. There have been few successful attempts using iron porphyrins incorporated into polymeric films and deposited onto electrode surfaces (2-3). These approaches were based on the finding that water-soluble iron porphyrins accelerate the reduction of nitrite in acid solutions (4) and on the fact that the polymeric structure may possess some of the properties of biological catalysts. In all the reported studies, it was suggested that the first step of the catalytic process involves the formation, in neutral aqueous solution, of an iron-nitrosyl complex as the consequence of the metal centered Fe^{III} /Fe^{II} reduction followed by nitrite binding, according to:

$[Fe^{III}]^+ + e^- \rightarrow [Fe^{II}]$, [1]

$[Fe^{II}] + HONO + H^+ \rightarrow [Fe^{II}(NO^+)]^+ + H_2O$, [2]

(where [Fe] symbolizes the iron heme center)

These steps are then followed by the reduction of the iron-nitrosyl adduct according to:

$[Fe^{II}(NO^+)]^+ + e^- \rightarrow [Fe^{II}(NO^{\cdot})]$ [3]

Besides few attempts, no direct evidence to fully characterize the above-cited reduction process and no accurate overall catalytic process were clearly established in the literature (2-5).

We herein report, for the first time, on a comparative study of the catalytic properties for the electroreduction of nitrite by didodecyldimethylammonium bromide DDAB surfactant films modified with hemin (Hm), myoglobin (Mb) and hemoglobin (Hb) to provide new insights in the analysis of this activation process in phosphate buffer solution at pH 7.4 (6).

For example, in the case of DAAB/Mb film, our results show for the first time a clear new indication on the first reduction process of the iron-nitrosyl adduct at potentials close to the Fe^{III}/Fe^{II} (≈ -0.15 V/*sce*). This process occurs at a potential nearly 1 V less negative that the well-known second multielectron reduction process (close to the Fe^{II}/Fe^{I} (≈ -1.15 V/*sce*)). This is clearly revealed by rotating disk electrode voltammetry (fig. 1), while it was not noticed in the previously reported studies conducted by cyclic voltammetry (5). Evidence for the formation of such an adduct comes from the fact that a decrease in the electrical charge due to the $Fe^{III} \rightarrow Fe^{II}$ reoxidation process is observed by cyclic voltammograms (6).

Analysis of the slopes of the Tafel plots for the reduction of nitrite at potentials close the Fe^{III}/Fe^{II} couple, with both DDAB/Hm and DDAB/Mb shows that the considered electrocatalytic process is a first-one electron transfer rate determining step. This indicates that the one-electron reduction of the iron-nitrosyl adduct (reaction [3]) is slow.

Analysis of the fractional reaction orders in nitrite is shown in Table 1. Even though, as yet, we have no suggestions to explain the signification of the fractional reaction orders calculated from the rotating disk electrode voltammetry data, these results clearly show that hemin and the heme groups in Mb (and also in Hb) behave differently, whereas the redox process (in the absence of nitrite) have similar potential values. This may be indicative of typical molecular recognition properties of the heme groups of the proteins.

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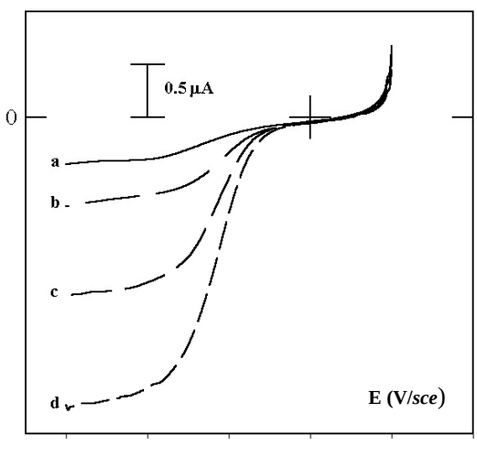

Fig.1. Rotating disk electrode voltammograms of DDAB/Mb film in the presence of nitrite in phosphate buffer solution (pH = 7.4) a: 2 mM; b: 4 mM; c: 6 mM; d: 8 mM (scan rate : 20 mV/s; rotation rate: 500 rpm).

Table 1. Reduction of nitrite on DDAB/Hm and DDAB/Mb films.

Film	Reaction order	
	1^{st} reduction (≈ -0.15 V/*sce*)	2^{nd} reduction (≈ -1.0 V/*sce*)
DDAB/Hm	0.19	0.24
DDAB/Mb	0.93	0.61